# Effects of methane outgassing on the Black Sea atmosphere

K. Kourtidis, I. Kioutsioukis, S. Rapsomanikis

Atmos. Chem. Phys. Discuss., 6, 3611–3626, 2006
www.atmos-chem-phys-discuss.net/6/3611/2006/


Atmospheric Chemistry and Physics Discussions

# Effects of methane outgassing on the Black Sea atmosphere

**K. Kourtidis, I. Kioutsioukis, and S. Rapsomanikis**

Lab. of Atmospheric Pollution and Pollution Control Engineering of Atmospheric Pollutants, Dept. of Environmental Engineering, Demokritus University of Thrace, 67100 Xanthi, Greece

Received: 7 February 2006 – Accepted: 2 March 2006 – Published: 9 May 2006

Correspondence to: K. Kourtidis (kourtidi@env.duth.gr)

## Abstract

Methane in air and seawater was measured in the Eastern Black Sea during the 10–18 December 1999 BIGBLACK project cruise. The measurements allowed for the calculation of supersaturation ratios and methane fluxes across the air-sea interface. $CH_4$ mixing ratios in air were generally in the 1.8–2.0 ppmv range, while surface (4 m depth) seawater concentrations varied from 5 to 100 ppmv. Above active seep areas, the water was supersaturated at around 500% with respect to the overlying atmosphere. Accordingly, flux densities varied greatly and were up to 4000 umol $m^{-2}$ $day^{-1}$. In the Sevastopol harbour, supersaturations up to around 3000%, similar to those at the Danube Delta, were observed, while in the Istanbul harbour supersaturations could not be determined because the very high values of water concentrations have led to detector saturation. Simple modelling shows that the observed fluxes do not have any substantial impact in the methane content of the Black Sea atmosphere, as they could only raise its concentrations by less than 1 ppb. On the other hand, calculations performed as part of the CRIMEA project, show that mud volcano eruptions could episodically raise the methane concentrations well above their regional background for several tens of kilometres downwind.

## 1 Introduction

Methane is an important greenhouse gas and a precursor of tropospheric ozone. It is produced in a variety of thermogenic and biological methanogenic processes, some of which occur on geologic time scales, while others on much shorter ones. As a result of these processes, large variations of atmospheric methane abundance might be expected, especially if large methane reservoirs become unstable. Such reservoirs include methane hydrates.

The Black Sea has received attention as a target of investigations on methane because of the large amounts of methane trapped in the anaerobic sediments and the



ACPD

6, 3611–3626, 2006

hydrates present underneath these sediments. Under normal conditions, methane is vented from the sediments to the overlying water; some of this methane reaches unoxidised the water-air interface and subsequently escapes to the atmosphere, although most of it is consumed from bacterial activity within the water column (e.g. Durisch-Kaiser et al., 2005).

Some investigations of the methane flux from the Black Sea to the atmosphere have already been carried out (Amouroux et al., 2002; Schmale et al., 2005), yielding flux densities generally between 0.19–0.77 nmol $m^{-2}$ $s^{-1}$ (16–66 umol $m^{-2}$ $day^{-1}$), while above active seeps these might increase to 0.96–2.32 nmol $m^{-2}$ $s^{-1}$ (83–200 umol $m^{-2}$ $day^{-1}$), and above river plumes it might increase even further, up to 5.44 nmol $m^{-2}$ $s^{-1}$ (470 umol $m^{-2}$ $day^{-1}$).

To derive these fluxes, Amouroux et al. (2002) and Schmale et al. (2005) used the Liss and Merlivat (1986) and the Wanninkhof (1992) parameterisations of the dependency of the transfer velocity $k$ on wind speed $u$, hereafter referred to as LM86 and W92, respectively. Both parameterisations are quadratic or near-quadratic; W92, for example, parameterises $k$ as a function of $u$ as $k=0.31\,u_{10}^2(S_c/660)^{-0.5}$, where $S_c$ is the Schmidt number of $CO_2$ in seawater, 660 is the $S_c$ for $CO_2$ in seawater at 20°C and $u_{10}$ is the wind speed corrected to 10 m height under neutral conditions.

Recent work, based to a large extend on measurements performed during the GasEx-1998 field experiments (McGillis et al., 2004), has resulted in other, cubic parameterisations, which yield better fits to the data (e.g. Hare et al., 2004, and references therein). Wanninkhof and McGillis (1999), using recent laboratory and field studies, proposed a cubic relationship between air-sea gas exchange and wind speed, $k_{660}=0.028\,u_{10}^3$, or $k=0.0283\,u_{10}^3(S_c/660)^{-0.5}$), which, compared with previous calculations using the W92 parameterisation, resulted in a significant increase of the calculated oceanic global annual $CO_2$ uptake. Fairall et al. (2000) reviewed the theoretical basis of various parameterisation schemes for bulk-to-bulk gas transfer. Since then, McGillis et al. (2001) used eddy accumulation for $CO_2$ to determine $k$ and showed that $k$ can be described in their study as $k_{660}=3.3+0.026\,u_{10}^3$, where $k_{660}$ is the $k$ nor-



ACPD
6, 3611–3626, 2006



EGU

malised to $S_c$ of 660 in cm hr$^{-1}$ (which equals the $S_c$ for $CO_2$ in seawater at 20°C). Other recent work used measurements of dual tracers during the Southern Ocean Iron Fertilisation Experiment SOFex (Wanninkhof et al., 2004), addressing the discrepancies between observational and model-based estimates of $CO_2$ uptake in the Southern Ocean (see also Feely et al., 2004), considered the effect of wind speed products (Olsen et al., 2005) and addressed the effects of sea-state dependent wave breaking (Woolf, 2005).

In the present study, we applied LM86, W92 and additionally, the more recent parameterisation of McGillis et al. (2001), hereafter referred to as MG01, to determine the flux of methane across the sea-air interface using cruise data. LM86, W92 and MG01 normalise their parameterisations with respect to the $S_c$ of $CO_2$ in seawater at 20°C. Schmidt numbers for methane and $CO_2$ are rather similar, their difference being –1.7% to 2.6% in the temperature range 0 to 20°C. Hence LM86, W92 and MG01 parameterisations can be used for methane without modification and without introducing a significant error, since the uncertainty in $S_c$ ranges from 3% to 10%, mainly due to uncertainties in the diffusion coefficient. We note also here that while LM86 note 600 as the $S_c$ of $CO_2$ at 20°C, W92 and MG01 note 660 as the $S_c$ of $CO_2$ at 20°C. However, $k$ being a function of either $(S_c/600)^{-0.5}$ or $(S_c/660)^{-0.5}$ (Watson et al., 1991, and references therein), the error from this convention is less than 5%.

## 2 Experiment and methods

The BIGBLACK cruise took place in the waters of the Western Black Sea, in the longitude range 29–32° E and the latitude range 42–45.5° N, onboard the Russian R/V Professor Vodianitsky.

Methane in air and seawater was measured with an automated Shimadzu GC/FID equipped with a Weiss equilibrator (Weiss, 1981). Details on the experimental setup can be found in Bange (1994) and Bange et al. (1994), while more details on the function of the equilibrator, as well as a mathematical treatment of the equilibrating

processes can be found in Butler et al. (1988, 1989). Briefly, the analysis was performed isothermally on a mol sieve 5Å column at 50°C, with an injector temperature of 60°C and a detector temperature of 280°C. A 10-port valve with two sample loops was used to inject the sample, which was dried before entering the analytical system by means of a 30-cm glass tube filled with Sicapent drying agent. Sampling alternated between ambient air and equilibrated air. Two $CH_4$ standards from Messer-Griesheim (of 1.57 and 1.96 ppmv methane) were used to calibrate the system during the cruise. Eight duplicate readings from alternate analyses of the two standards gave a response ratio of 1.244±0.012 ($1\sigma$), practically identical to the nominal manufacturer's concentration ratio of 1.248. Hence, the first standard, of 1.96 ppmv $CH_4$, was used extensively throughout the cruise (two to five calibrations daily), while the second one, of 1.57 ppmv $CH_4$ was used only during 17 December 1999. The reproducibility of the measurements, as determined from multiple standard injections during the course of each day, was around 1%.

The inlet for air analyses was around 50 m long, while the inlet from the equilibrated air was around 4 m long. Multiple runs under operating conditions with the 1.96 ppmv methane standard connected to both inlets showed no significant differences that might have risen from inlet wall losses between the two inlets (i.e. the differences were within the 1% reproducibility limits).

The duplicate readings from two different sample loops provided us with the confidence that the precision to see significant local increases in atmospheric concentrations due to high methane fluxes was more than adequate.

Methane supersaturations and fluxes were calculated from measurements using the methodology described in detail in Bange (1994) and Bange et al. (1994, 1996), which is based on the approach of Liss and Merlivat (1986) (LM86), for the transfer velocity calculation. Fluxes were also calculated with the W92 and the MG01 parameterisation. Water temperature and salinity at 4 m (the depth where the water pump inlet was located) were measured with CTD sondes during the cruise. The deviations ($1\sigma$) of these two parameters during the cruise were small (temperature: 10.68±0.29, salinity



ACPD
6, 3611–3626, 2006



EGU

17.6±0.34), hence their mean values were used in all calculations. Two pressure-equilibrating tubing lines in the equilibrator ensured sampling under atmospheric pressure, hence no pressure correction had to be applied.

We also established that the equilibration time of the seawater equilibrator (around 15 min) might have caused, in the case of rapidly fluctuating concentrations, a smoothing of the measured seawater concentrations while sampling en route. This does not affect the measurements performed to the stations visited during the cruise (Danube fan, active seeps and Sevastopol harbour). Furthermore, the system performed without any problems for the duration of the cruise and we were able to calculate supersaturation ratios and fluxes of methane from the cruise area to the atmosphere.

The model used for calculating the dispersion of the methane plume from mud volcano eruptions is the 3-D airshed model ISC-AERMOD-VIEW from Lakes Environmental Inc., modified to accommodate a larger grid (original grid 50 km×50 km). The model calculated the concentrations at 100×100 receptors at grid points and is based on the US EPA ISCST3 dispersion model for inert pollutants.

Required inputs are the wind velocity (8 m/s, 1.5 m/s for stability class A) and direction (various), relative humidity (60%), temperature (288 K), pressure (1024 mb) and stability class (D, F and A). The mixing height was set to 1000 m.

## 3 Results and discussion

The measurements of methane in air and seawater, together with the calculated supersaturation ratios, are presented in Figs. 1 and 2. The ship left the harbour of Istanbul on 9 December. Very high values of methane in air equilibrated with seawater lead to the saturation of the FID detector of the analytical system, hence inhibiting quantitative determination of the very high methane seawater supersaturations while in the harbour. Further, upon departure of the ship, the propeller caused sediment to enter the system; hence the measurements were resumed, after extensive cleaning, on 10 December. On 10 December, the ship sampled en route as well as over an active seep area. On



ACPD
6, 3611–3626, 2006

11 December, the Danube fan area was sampled. On 13 December, the whole day was spent above an active seep. The ship entered the port of Sevastopol early in the morning of 16 December, where measurements continued until the afternoon of 17 December.

Above the two active seep areas where the ship sampled on 10 and the entire 13 December, methane concentrations in seawater were 8–20 ppmv, resulting in supersaturation ratios 200–600%. In the Danube fan area, where the ship sampled on 11 December, methane concentrations in seawater were up to 92 ppmv, resulting in supersaturation ratios of up to nearly 3000%, In the Port of Sevastopol, where the ship sampled on 16 and 17 December, methane concentrations in seawater were 50–92 ppmv, resulting in supersaturation ratios 1500–3000%, higher than in the active seep areas. In the port of Istanbul, methane concentrations in seawater were even higher than in Sevastopol, but could not be quantified because the detector reached saturation.

Flux densities (Fig. 3), as already mentioned, were calculated using the methodology described in detail in Bange (1994) and Bange et al. (1994), using the parameterisations of the dependency of the transfer velocity on wind speed of LM86, W92 and MG01 (see Introduction). Lacking wind speed and salinity measurements during the ship's stay in the port of Sevastopol, flux densities were not calculated, but they should obviously be higher than above active seeps. Quite high flux densities were also calculated for the Danube fan area. Generally, flux densities are higher than the ones obtained in our group's cruise in the same area during July 1995 (Amouroux et al., 2002). In open and shelf waters, Amouroux et al. (2002) measured flux densities 50–53 umol $m^{-2}$ $day^{-1}$ (calculated with W92), while the measurements reported here range between 23–280 umol $m^{-2}$ $day^{-1}$, with a mean around 100 umol $m^{-2}$ $day^{-1}$ (calculated also with W92) for open and shelf waters. However, the measurements during the present study above the active seep area during the station there at 10 December fluxes were 240–716 umol $m^{-2}$ $day^{-1}$ and measurements above the Danube fan on 11 December were up to 3943 umol $m^{-2}$ $day^{-1}$ (W92). At the high wind speeds of 11 and 12 December (up to 6 m/s), differences are observed between the cubic (LM86)



ACPD
6, 3611–3626, 2006

and the quadratic parameterisations (MG01 and W92), the latter increasing the calculated wind densities by approximately a factor of two (Fig. 3), while at low wind speeds substantial differences (up to a factor of two) result also between MG01 and W92, the former being higher.

We used a simple method to estimate the effects of the above fluxes on the air concentrations of $CH_4$: We assume a box located above the sea, with its ceiling at 1000 m, which appears a reasonable assumption for the height of the mixing atmospheric layer. The box is ventilated by the horizontal wind, for which we use the values that were measured during the BIGBLACK cruise onboard R/V Professor Vodianitsky (as measured, otherwise 8 m/s). If we assume that methane is vented into the box with the flux densities of Fig. 3 (LM86), and the contents of the box are vented completely out of the box in the time required for the mean wind speed to cross the box from one side to the other, with a series of simple calculations we derive that the measured flux densities would result in an increase in the atmospheric mixing ratio of methane by the amounts given in Fig. 4. Even if we use a different parameterisation, the increases would not exceed a few hundreds pptv.

Clearly, under normal conditions the air-sea exchange of methane from the Black Sea has a negligible impact on the regional atmospheric background of methane, being many times smaller than the observed variability of atmospheric methane (Fig. 1b).

We now examine the case of episodic outbursts due to mud volcano eruptions. Following results from recent work on bubble-water column exchange of gases in the frame of the CRIMEA project (Daniel McGinnis, FZL-EAWAG, Switzerland; unpublished data), we assume in the worst case that 0.1% of the methane gas might reach the atmosphere, provided the eruption occurs at relatively shallow depths. In other words, a small fraction of methane bubbles rise all the way from the sea floor to the sea surface, passes the pycnocline and then releases to the atmosphere, where it also self-ignites. We assume the release occurs from a rectangular area source 100 m × 100 m, hence the emission rate in this case is 6.25 mmol $m^{-2}$ $s^{-1}$ (Guliyiev and Feizullayev, 1994).



ACPD
6, 3611–3626, 2006

Our modelling suggests (Fig. 5) that methane outbursts from mud volcanism (provided some 0.1% of the methane gas reaches the atmosphere) may result in very large enhancements in the regional methane concentrations near the sea surface. For unstable and neutral conditions, the release results in raising the atmospheric methane concentration by 1–40 ppmv in the first 5 km from the release site, falling off at greater distances. Under nighttime stable conditions, the enhancement can reach 600 ppmv close to the source, creating smog chamber conditions. The larger computed increases propagate also at larger distances (for 30 km downwind methane is increased by more than 7 ppmv, falling to its atmospheric mixing ratio of 1.8 ppmv after 50 km). Given that the dispersion model is linear (i.e. a doubling of the emission rate will double the concentrations), if a larger proportion of the methane reaches the atmosphere, concentrations will be proportionally larger.

Even with the modest 0.1% amount of the emitted methane reaching the atmosphere, some of the modelled increases are well above the sensitivity of available instrumentation, also space-borne (e.g. SCIAMACHY on ENVISAT), providing perhaps a means for indirect sensing of mud volcano eruptions.

*Acknowledgements.* This work was funded under the BIGBLACK (EU IC15 CT96 0107) and CRIMEA (EVK-2-CT-2002-00162) European Commission projects.

## References

Amouroux D., Roberts G., Rapsomanikis, S., and Andreae, M. O.: Biogenic Gas ($CH_4$, $N_2O$) Emission to the Atmosphere from Near-shore and Shelf Waters of the North Western Black Sea, Estuarine, Coastal and Shelf Science, 54(3), 575–587, 2002.

Bange, H. W., Bartell, U. H., Rapsomanikis, S., and Andreae, M. O.: Methane in the Baltic and North Seas and a reassessment of marine emissions of methane, Global Biogeochem. Cycles, 8, 465–480, 1994.

Bange, H. W.: Messungen von Lachgas ($N_2O$) und Methan ($CH_4$) in Europaeischen Nebenmeeren, PhD Thesis, Johannes Gutenberg-Universitaet, Mainz, 1994.

Bange, H. W., Rapsomanikis, S., and Andreae, M. O.: The Aegean Seaa as source of atmospheric nitrous oxide and methane, Marine Chemistry, 53, 41–49, 1996.
Butler, J. H., Elkins, J. W., Brunson, C. M., Egan, K. B., Thompson, T. M., Conway, T. J., and Hall, B. D.: Trace gases in and over the West Pacific and East Indian Oceans during the El Nino-Southern Oscillation event of 1987, NOAA Data Report ERL ARL-16, Air Resources Laboratory, Silver Spring, MD, USA, 1988.
Butler, J. H., Elkins, J. W., Thompson, T. M., and Egan, K. B.: Tropospheric and dissolved $N_2O$ off the West Pacific and Indian Oceans during the El Nino-Southern Oscillation event of 1987, J. Geophys. Res., 94, 14 865–14 877, 1989.
Durisch-Kaiser E., Klauser, L., Wehrli, B., and Schubert, C.: Evidence of intense archaeal and bacterial methanotrophic activity in the Black Sea water column, Appl. Environ. Microbiol., 71, 8099–8106, 2005.
Fairall, C. W., Hare, J. E., Edson, J. B., and McGillis, W.: Parameterisation and micrometeorological measurements of air-sea gas transfer, Boundary-Layer Meteorol., 96, 63–105, 2000.
Feely, R. A., Wanninkhof, R., McGillis, W., Karr, M.-E., and Cosca, C. E.: Effects of wind speed and gas exchange parameterisations on the air-sea $CO_2$ fluxes in the equatorial Pacific Ocean, J. Geophys. Res., 109, C08S03, doi:10.1029/2003JC001896, 2004.
Guliyiev, I. S. and Feizullayev, A. A.: Natural hydrocarbon seepages in Azerbaijan, Proc. AAPG Hedberg Research Conference, April 24–28, Vancouver, Canada, pp. 76–79, 1994.
Hare, J. E., Fairall, C. W., McGillis, W. R., Edson, J. B., Ward, B., and Wanninkhof, R.: Evaluation of the NOAA/Coupled-Ocean Atmopheric Response Experiment (NOAA/COARE) air-gas tranfer parameterization using GasEx data, J. Geophys. Res., 109, C08S11, doi:10.1029/2003JC001831, 2004.
Liss, P. S. and Merlivat, L.: Air-sea exchange rates: introduction and synthesis, in: The role of air-sea exchange in geochemical cycling, edited by: Buat-Menard, P., 113–127, Reidel, D., New York, 1986.
McGillis, W. R., Edson, J. B., Ware, J. D., Dacey, J. W. H., Hare, J. E., Fairall, C. W., and Wanninkhof, R.: Carbon dioxide flux techniques performed during GasEx-98, Marine Chem., 75, 267–280, 2001.
McGillis, W. R., Asher, W. E., Wanninkhof, R., Jessup, A. T., and Feely, R. A.: Introduction to special section: Air-sea exchange, J. Geophys. Res., 109, C08S01, doi:10.1029/2004JC002605, 2004.
Olsen A., Wanninkhof, R., Trinanes, J. A., and Johannessen, T.: The effect of wind speed

products and wind speed-gas exchange relationships on interannual variability of the air-sea $CO_2$ gas transfer velocity, Tellus, 57B, 95–106, 2005.
Schmale, O., Greinertand, J., and Rehder, G.: Methane emission from high-intensity marine gas seeps in the Black Sea into the atmosphere, Geophys. Res. Lett., 32, L07609, doi:10.1029/2004GL021138, 2005.
Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res., 97(C5), 7373–7382, 1992.
Wanninkhof, R. and McGillis, W. R.: A cubic relationship between air-sea $CO_2$ exchange and wind speed, Geophys. Res. Lett., 26, 1889–1892, 1999.
Wanninkhof, R., Sullivan, K. F., and Top, Z.: Air-sea gas tranfer in the Southern Ocean, J. Geophys. Res., 109, C08S19, doi:10.1029/2003JC001767, 2004.
Watson, A. J., Upstill-Goddard, R. C., and Liss, P. S.: Air-sea gas exchange in rough and stormy seas measured by a dual-tracer technique, Nature, 349, 45–147, 1991.
Weiss, R. F.: Determinations of carbon dioxide and methane by dual catalyst flame ionisation chromatography and nitrous oxide by electron capture chromatography, J. Chromatogr. Sci., 19, 611–616, 1981.
Woolf, D. K.: Parametrization of gas transfer velocities and sea-state-dependent wave breaking, Tellus, 57B, 87–94, 2005.

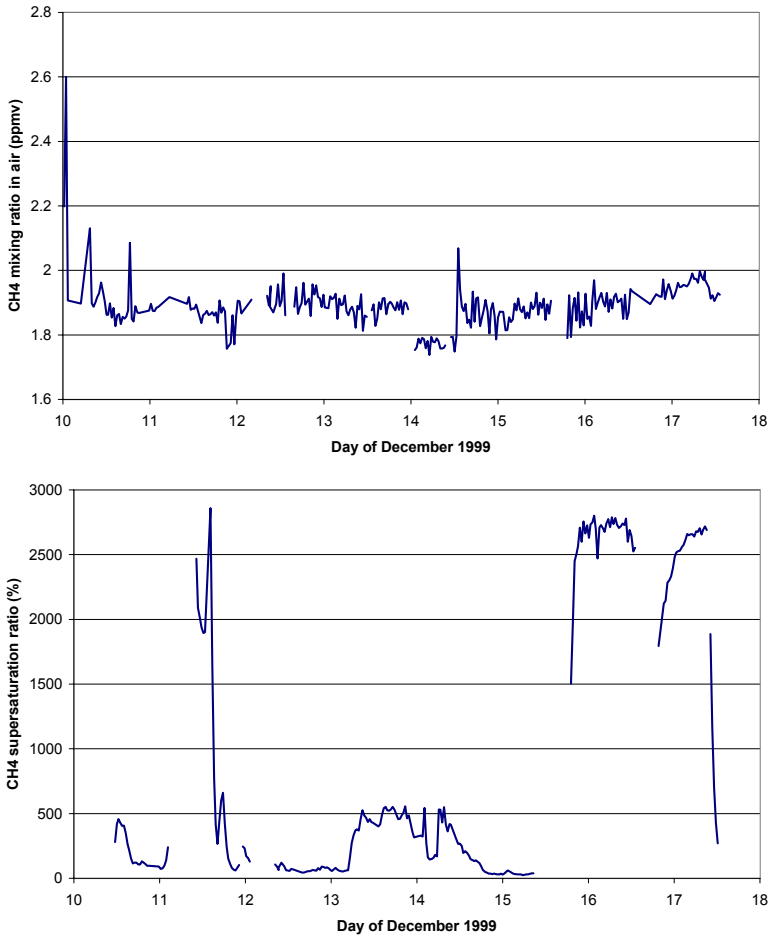


**Fig. 1.** Methane mixing ratios (above) in air and supersaturation ratios (below) during the BIGBLACK cruise.



ACPD
6, 3611–3626, 2006

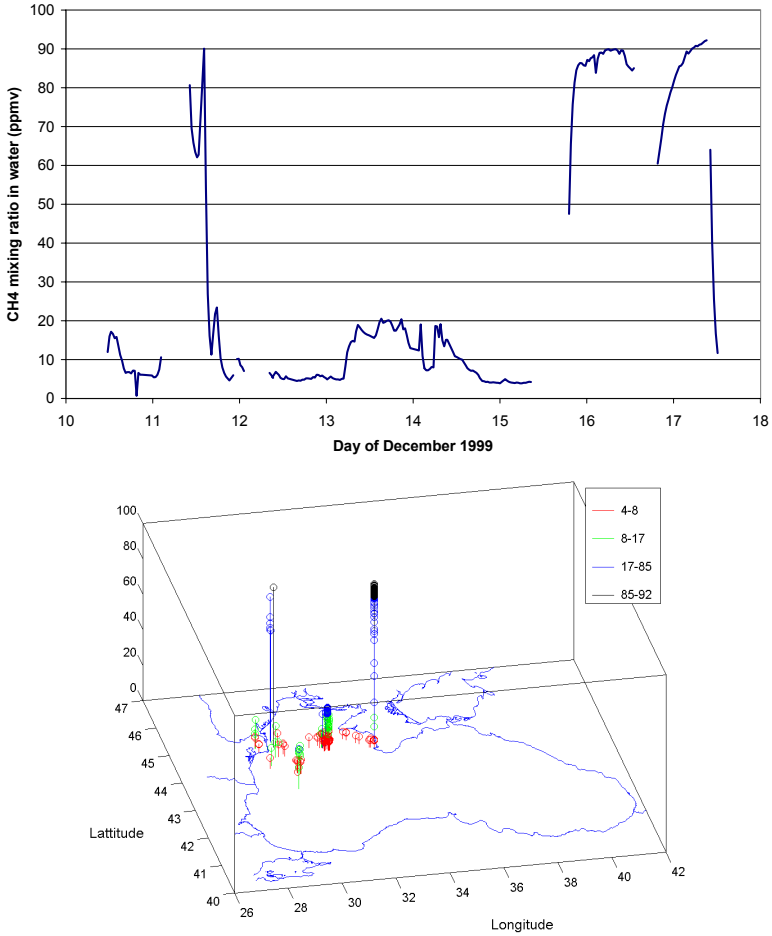


**Fig. 2.** Methane mixing ratios in water (in ppmv) during the BIGBLACK cruise plotted as a function of date (above) and as a function of position (below). The 1:250 000 resolution coastline is from NOAA's National Geophysical Data Centre.



ACPD
6, 3611–3626, 2006



EGU

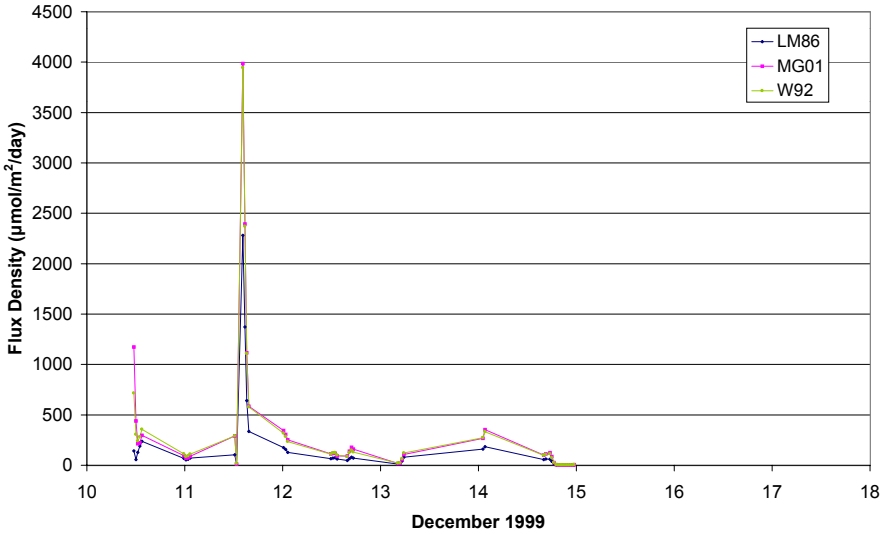


**Fig. 3.** Flux densities calculated after LM86, W92 and MG01.

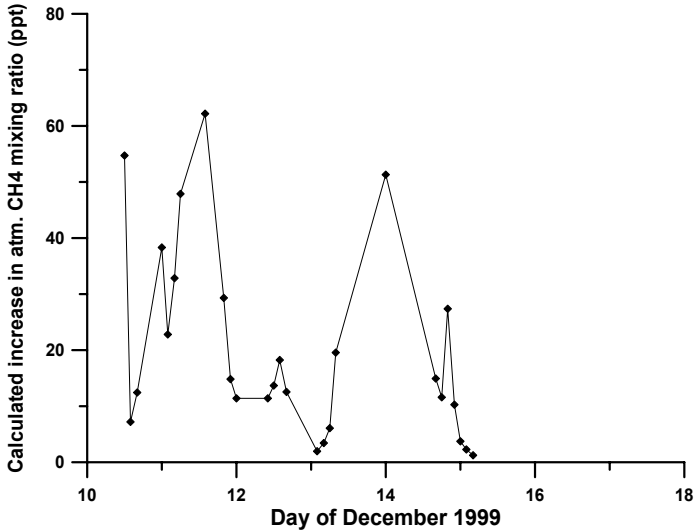


**Fig. 4.** Calculated increases in the atmospheric methane concentration due to the measured fluxes (using the LM86 parameterisation). See also text.



ACPD
6, 3611–3626, 2006

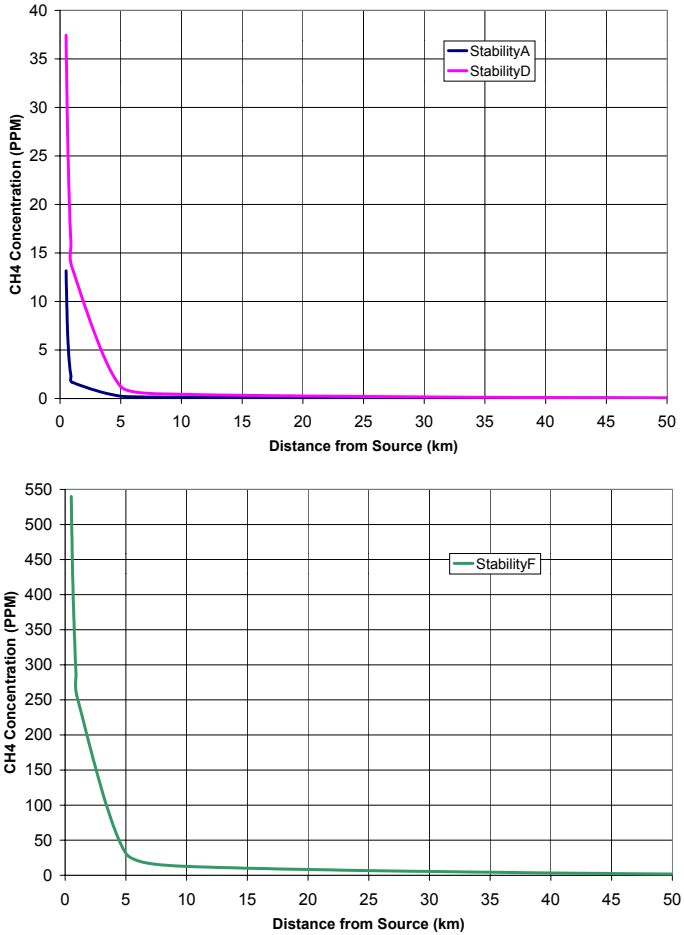


**Fig. 5.** Methane plume dispersion from episodic *unignited* outbursts for unstable-neutral (top) and stable (bottom) atmospheric conditions.



ACPD
6, 3611–3626, 2006